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Short communication

Interactions between vitrinite and inertinite-rich coals and the ionic liquid – [bmim][Cl]

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ABSTRACT

The interactions between vitrinite and inertinite-rich coals and the ionic liquid butylimidazolium chloride ([bmim][Cl]) heated to 100 °C have been characterised. Differences in the interactions of coal macerals and ionic liquids have been identified. [bmim][Cl] is able to dissolve 22 wt% of a high-vitrinite coal fraction compared to 14 wt% of a high-inertinite coal fraction. The vitrinite-rich coal fraction tends to swell to a greater extent compared to the inertinite-rich coal fraction, which was fractured and fragmented rather than swelled.

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1. Introduction

Coal is a sedimentary rock composed primarily of macerals, some minerals, and water and gases in sub-microscopic pores. Coal is not simply carbon, hydrogen, oxygen, sulfur, and minor proportions of other elements; nor is it, as is often implied, a uniform, poly-aromatic substance. Rather, coal is an aggregate of microscopically distinguishable, physically distinctive, cross-linked and chemically different macerals and minerals [1]. Coal macerals such as vitrinite, inertinite and liptinite are organic substances derived from plant tissues that have been decayed to different extents, incorporated into sedimentary strata, and then compacted, hardened, and chemically altered by geological processes. Higher fluidity and lower physical density are observed in the cases of vitrinite and liptinite-rich maceral fractions. Vitrinite contains voluminous long aliphatic chains and bridges, and a significant number of substituents on aromatic rings. In contrast, inertinite-rich macerals have almost no fluidity and higher physical density, and have relatively high aromaticity.

Coal must undergo various pre-treatments for a number of industrial applications due to its cross-linked structures, aromaticity and low temperature volatiles, moisture and several forms of sulphur and chlorine together with inorganic minerals and trace elements [2]. Normally, coal is pre-treated thermally using torrefaction/pyrolysis [3] or with solvents solutions at elevated temperature, [4] depending on whether the purpose of refinement is to remove the impurities and volatiles or to fragment, disperse or dissolve the organic matter. To produce coal water slurry (CWS) fuel for diesel engine, hypercoal and ultraclean coal production, and coal to liquid (CTL) process, it is important to remove ash, volatile matter and other impurities associated with coal structure to improve the efficiency of process and to reduce environmental and operational problems. For coke making, carbon fuel cells, carbon and graphite rods for alumina and many other industries, pre-treatments at relatively high processing temperatures produces a strong, stable, solidified coal material. The current paper focuses on the use of ionic liquids (ILs) for the solvent extraction of coal.

The literature available on different coals and solvent interactions is extensive [4]. Solvent extraction has been used for even compositional characterization of coals [5]. Several existing coal refining processes also use solvent treatment at different temperatures along with pressurized hydrogen to facilitate some degree of desulfurization [6]. Pre-treatments for removal of mineral matter and modification of coal have also been reported [7]. The ultraclean coal project in Australia and hypercoal project in Japan have demonstrated efficient demineralization of coal by alkali solution and organic solvent extraction, respectively. Coal pre-treatment with methanol has also been reported for the improvement of selective grindability of organic substances and mineral matter in coal [8]. Coal pre-treatments with dilute acid solutions have been also reported for the enhancement of coal depolymerization,

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Table 1
Proximate and Ultimate analysis of the coal.

	Air dried basis (%)
Proximate analysis	
Air dried moisture	1.8
Ash	6.6
Volatile matter	18.6
Fixed carbon	73.0
Ultimate analysis	
Carbon	81.8
Hydrogen	4.35
Nitrogen	1.69
Total sulfur	0.38
Oxygen (by diff)	3.4

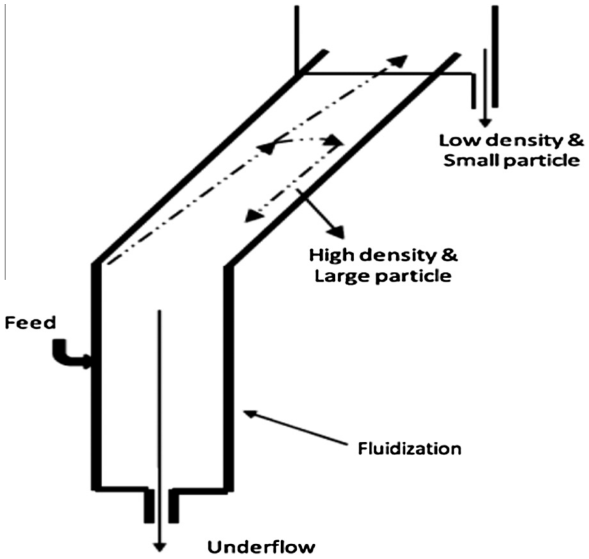

Fig. 1. Schematic of reflux classifier [18].

Table 2
Properties of the two selected samples with different macerals composition.

Coal samples	Particle size (μm)	Vitrinite (wt%)	Inertinite (wt%)	Ash (wt%)	Relative density (RD) in g/cc
A	106–212	85.42	14.58	3.23	1.35
B		50.2	49.8	14.92	1.57

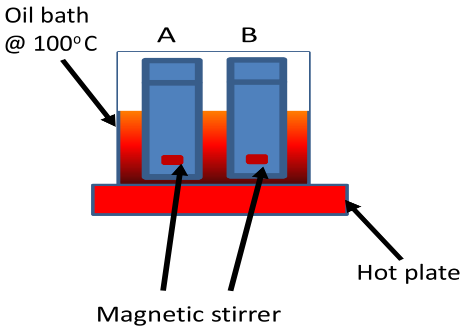

Fig. 2. Schematic of the experimental set up.

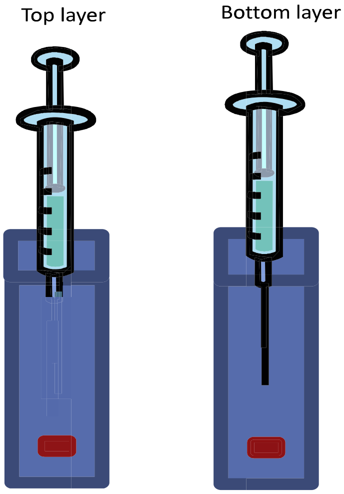

Fig. 3. Sampling for micrographs.

liquefaction, and pyrolysis reactions [9]. Nonpolar hydrocarbon solvents, such as toluene or hexane, although extensively studied, have limited ability to swell coals therefore extract only small amounts of soluble material. Conversely, solvents having strong hydrogen bonds acceptor groups, such as pyridine or N-methylpyrrolidinone (NMP), swell and dissolve coal particles. Degrading solvents, such as phenanthridine and anthracene have been used to fragment, disperse and dissolve coal [10]. Water is also used as a co-solvent for catalyst dispersion in many of the processes.

However, the cost of solvents, losses during their use, degradation, their recovery after use, long term performance and environmental hazards are major issues for practical applicability [11]. Therefore, the feasibility of replacing existing with solvents by green solvent such as ionic liquids (ILs) is investigated. ILs consist of large organic cations associated with various anions that melt below 100 °C [12]. They often exceptional chemical and thermal stability and are normally found to be non-flammable at ordinary temperatures [13]. They also generally have negligible vapour pressure, thereby reducing evaporative losses during IL properties can be “tuned” by varying substituent groups of cations and anions, [14,15] so that unusual combinations of reagents, both organic and inorganic, can be formulated. The solubility of kerogen and oil shale has been studied in the ILs in 1990s [16]. In recent biomass based studies for biomass to liquid process, it is observed that hydrophilic ILs dissolves cellulose and hydrophobic dissolves lignin structures from biomass [16]. Recently, Painter et al. [17] studied dispersion and dissolution of coal in to different ILs. It was concluded that only certain ILs was able to disperse and fragment some coals. However, the science behind the interactions of different coals and ILs is still not properly understood.

Our hypothesis is that the fragmentation, dispersion and dissolution of different coals into ionic liquids may be coal macerals specific. Therefore, vitrinite and inertinite-rich coal fractions have been studied in this paper to better understand their interactions with ionic liquids.

2. Coal macerals separation and ionic liquid selection

The proximate and ultimate analysis of the studied coal is given in Table 1. Coal maceral fractions were separated using reflux classifier technique, which operates on the principle of particle settling rates within an inclined plane. This technique has been developed and successfully employed for mineral and coal particles separation by Galvin et al. [18–20]. The reflux classifier set-up is

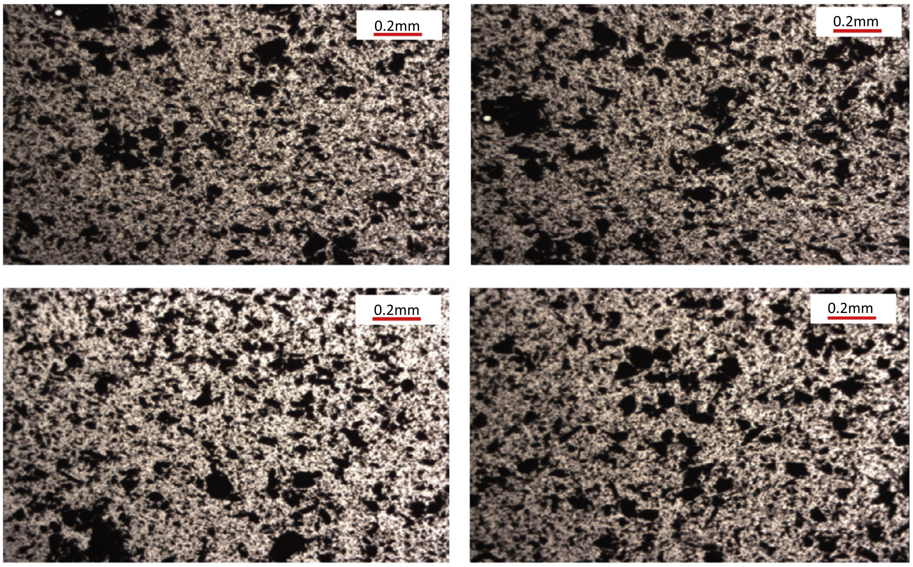

Fig. 4a. Optical micrographs for coal sample A (top layer).

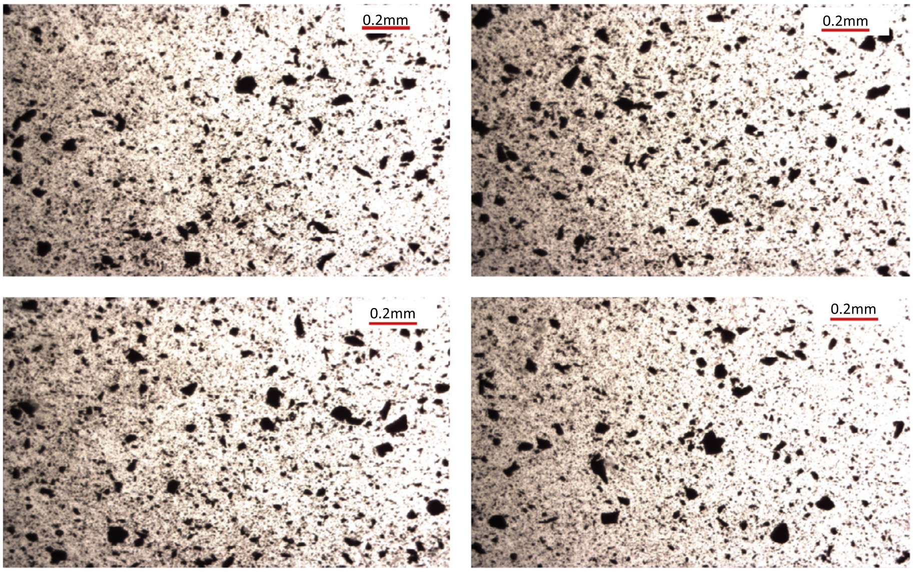

Fig. 4b. Optical micrographs for coal sample B (top layer).

a combination of a system of parallel inclined channels above a conventional fluidized bed, as shown in Fig. 1 [18,19].

During coal maceral separation, the coal slurry feed is plunged downwards into the vessel, forming a bed of coal particles that is fluidized by water from below. The fluidized suspension passes up into the inclined channels, where particles are segregated onto the upward facing surfaces of the inclined channel. Lighter, less dense, smaller particles have the slowest settling rate and are removed first as overflow. Successive increases in water flow rate remove higher density particles.

Under a typical fluidization controlled by water flow rate, coal particles either were conveyed upward out of the inclined channel with water or slid down back into the fluidized bed, depending on the density and particle size. Therefore, coal particles of a given density and size would be separated at a typical water flow rate. Detailed description on the reflux classifier operation is described elsewhere [19]. The coal maceral fractions A and B derived from the reflux classifier exercise as highlighted in Table 2 were selected for the IL experiments. The samples were dried and sieved further to a size fraction of 106–212 μm.

Butylimidazolium chloride ([bmim][Cl]) (RD = 1.23 g/cc) was selected as the ionic liquid for study based on prior results [17]. In this previous study, several imidazolium based ionic liquids (i.e. [bmim][Cl], [bmim][BF_4], [bmim][CF_3SO_3] and [bmim][PF_6]) were investigated for the effectiveness for dispersion and dissolution of Port river basin (PRB), Illinios no. 6 and Upper Freeport coals. Of all the ionic liquids, [bmim][Cl] was most effective for fragmenting and dissolving PRB coal; [bmim][Cl] dissolved nearly 19% of PRB coal in two hours of mixing at 100 °C, significantly higher than for the same coal with pyridine and from N-methylpyrrolidinone (NMP). Further, ionic liquids interactions with coal were highly selective; an IL that was effective for processing one type of coal was ineffective for another. In this work a link between the ionic liquid and coal macerals is established to address selective performance of ionic liquids for coal extraction.

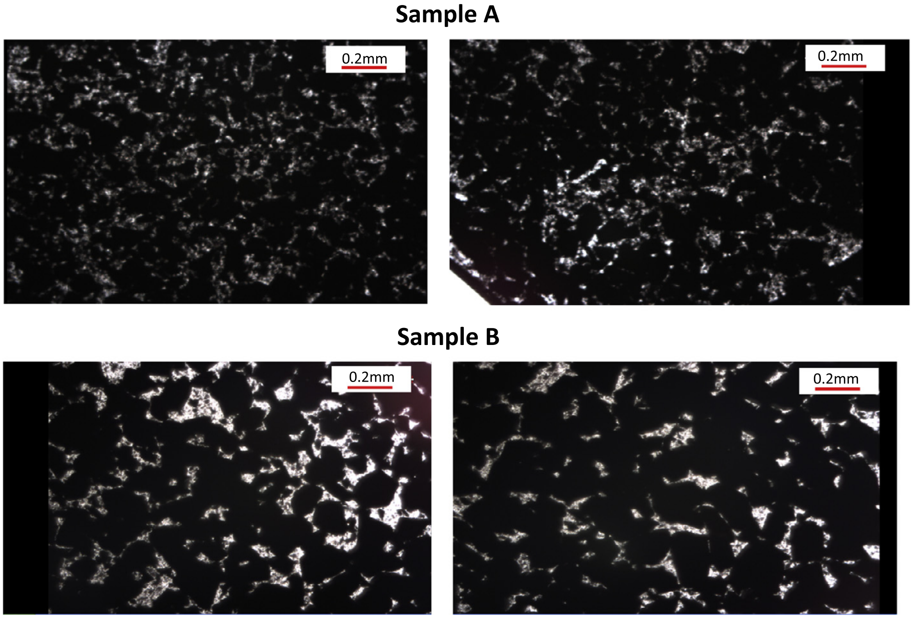

Fig. 5. Optical micrographs for coal samples (bottom layer).

3. Experimental

The [bmim][Cl] with 99% purity was purchased from Sigma–Aldrich and used as-received. The coal sample cuts A and B derived using reflux classifier were used in these experiments. Around 20 mg of coal samples A (vitrinite-rich) and B (medium vitrinite-rish and high inertinite-rich) were mixed with [bmim][Cl] in a sample tube (i.e. 30 vol% coal in [bmim][Cl]) with magnetic stirrer and kept at 100 °C in an oil bath for around 3 h as shown in Fig. 2.

After experiments, droplets of samples were smeared onto glass slides at room temperature for microscopic evaluation. The droplets from the top and bottom layer of the sample tube were sucked by a syringe as shown in Fig. 3.

Due to the larger size of the syringe top and smaller opening of sample tube, the bottom layer was obtained using a needle. Micrographs were obtained in transmission using a LeicaDM 4000 research microscope. Micro-syringe filters were used to separate the undissolved coal and a mixture of dissolved coal and ionic liquid. The fragmentation and dispersion of the coals into [bmim][Cl] was analysed from micrographs while the dissolution was calculated based on the separation of undissolved coal and a mixture of dissolved coal and [bmim][Cl]. The coal samples used in the current experiments were around 20 mg and therefore further analysis of the recovered undissolved coal as well as resultant coal+IL mixture was not performed.

4. Results and discussion

[bmim][Cl] melts at 80 °C. Upon heating [bmim][Cl] to 100 °C with coal for 3 h, a dark black dispersion was obtained. Upon cooling to room temperature, this suspension became more viscous, but did not solidify. To avoid gel formation when exposed to moisture from the atmosphere, the sample tube was kept well sealed. Optical micrographs obtained from the top layers are shown in Figs. 4a and 4b for coal samples A and B respectively. Four different micrographs were taken to reveal the mixture homogeneity in the top layer. The vitrinite -rich coal in sample A behaved differently to the medium vitrinite and high inertinite-rich coal in sample B.

A clear fluid is observed for coal sample A in Fig. 4a. The coal particles have swelled and are fluid, which clearly indicates that vitrinite -rich coal has become soft when in contact with the [bmim][Cl] for around three hours at 100 °C. In contrast, fragmentation is observed in Fig. 4b for coal sample B, with almost no swelling. Fine particles (<75 μm) are observed in the micrograph samples which indicates that inertinite-rich material ends to fragment rather than swell in the presence of [bmim][Cl]. These differences in the way the ionic liquid interacts with the two macerals suggests a means for selectively dissolving different coals through use of appropriate ionic liquids.

Aggregates of the coal more than 212 μm were observed for both coal samples in the bottom layer micrograph, c.f. Fig. 5. This is consistent with the softening both coal macerals types. Nonetheless, sample A, with has higher vitrinite content, is softer than the higher inertinite material.

It was difficult to accurately measure the dissolution of coal samples into [bmim][Cl]. Estimates were made by using a Teflon fiber micro-syringe filter and heated samples. Samples were filtered hot, and then the supernatant was removed, followed by re-dispersion with IL and repeated filtering and re-dispersion. Using this method it was estimated that approximately 22 wt% of coal A and 14 wt% of coal B was dissolved in [bmim][Cl]. The experiments were repeated for three times to ensure reproducibility.

[bmim][Cl] is effective for dissolving both high vitrinite and inertinite-rich coals. However, it is selective for high vitrinite coals, likely due to structural epitaxy between the ionic liquid and the vitrinite coal. Because [bmim][Cl] is able to swell this type of coal, it may dissolve the long aliphatic chains and bridges, and solubilizes the trapped organic and minerals. For high inertinite coal, fracturing or fragmentation occurs due to surface tension effects. Additionally, chemical reactions of aliphatic and aromatic components may occur.

To understand this interesting and selective behaviour of ILs in more detail advanced coal analysis techniques should also be employed in future. To assess the applicability of ionic liquids for larger scale extraction, larger batch sizes will be used and TGA analysis of the recovered undissolved coal and Matrix Assisted Laser Desorption & Ionisation Time of Flight Mass Spectrometry (MALDI-TOF-MS) analysis of the dissolved coal tars will be completed. HNMR, FTIR and petrography analysis will also be employed in future to reveal the composition of the coal and coal+IL mixture. This improved understanding on such will allow ILs to be selected or designed to specifically solubilize minerals or organic materials from different types of coals.

5. Conclusion

The interactions between high vitrinite and inertinite-rich coals and the ionic liquid [bmim][Cl] were investigated. The ionic liquid and the coal were heated in a sample tube at 100 °C for three hours which led to fragmentation, dispersion or dissolution of different coal macerals. [bmim][Cl] dissolved 22 wt% of the high-vitrinite coal compared to 14 wt% of the high inertinite coal. The higher vitrinite coal also swelled more in the presence of the ionic liquid compared to the inertinite-rich coal. The fact that the ionic liquid interacts differently with the different coal macerals suggests a means for selectively dissolving different coal types by tuning the structure of the ionic liquids. This could produce a performance advantage that makes coal extraction using ionic liquids economically feasible in the future.

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